

Non-Convergent Perturbation Theory and Misleading Inferences about Parameter Relationships: the Case of Superexchange

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Abstract

We discuss the well-known three-center cation-anion-cation model for superexchange in insulating transition-metal compounds using limiting expansions for the Anderson-Hubbard model. We find that due to the three interfering energy scales in the model, a limiting expression for the superexchange J for the idealized Mott-Hubbard (M-H) case $t \ll U \ll \Delta$ cannot be formally defined. We further show that no single expansion variable can describe any type of limiting behaviour for superexchange. The well-known t^4 expression for M-H insulators, obtained from path-dependent series expansions, is not unique to these systems as it can also be obtained with many other different expansions, in which either the $d - p$ energy difference Δ or the d -electron correlation U can actually be small. At times, and particularly for milder relationships between the parameters, $t \lesssim U \lesssim \Delta$, the reverse form of the series expansions can yield better agreement with the exact results. This implies that the fitting of experimental data to the simple expressions derived from path-dependent series expansions can lead to qualitatively incorrect relationships between the parameters, fictitiously within the M-H regime.

Keywords: Series expansions, Mott-Hubbard insulators, Effective Hamiltonians

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1. Introduction

The problem of superexchange, or the exchange interaction of two separated electron spins, is an old one, dating back *e.g.* to the work of Anderson [1] who obtained a simple expression for describing the interaction of $3d$ spins in Mn cations separated by a filled shell of O $2p$ electrons. Since then the concept has been applied to the estimation of parameters in a wide variety of systems, such as hopping parameters in transition-metal compounds, [2, 3] high T_c superconductors, [4] and electron transfer rates in donor-acceptor systems, such as radical pairs in biological molecules [5]. Following Anderson, many works in the literature have presented slight modifications and extensions of the superexchange expression J [6–9]. Experimentally, the electronic parameters cannot all be measured directly. Some studies, [10, 11] which rely on assumed models in order to fit experimental data on exchange, typically obtained from spin-wave [12, 13] or magnetic-susceptibility measurements [14] (for a review of experiments see Ref. [15]), are biased by the suitability of the model. In contrast, some other analyses, which fit photoemission spectra to parameters from cluster models [16–18], constitute an independent approach to obtaining values for the electronic parameters.

Indeed it has been shown, based on cluster model calculations including a full description of configuration interactions, that the late $3d$ transition-metal oxides should not be characterized as Mott-Hubbard (M-H) insulators, in which the energy gap is determined by the $d-d$ electron correlation U on the metallic species. Instead, these systems have been reclassified as charge-transfer (C-T) insulators [16, 17] in which the gap is determined by the energy of charge-transfer Δ between metal and insulator species. Similarly, as a result of comprehensive cluster calculations, the early transition-metal oxides are now considered to be at least intermediate between the two regimes, with some classified as C-T [18].

In this paper we rederive the well-known problem of the superexchange interaction of singly-occupied cations in a three-site cluster model as a proof-of-principle that expressions for limiting forms are generally path-dependent

whenever multiple energy scales are present. This concept is generalizable to the plethora of other problems in physics described by multiple energy scales and for which analytical expressions are only available in limiting forms.

Obtaining a simple expression for complex quantities often relies on series
 35 expansions. A careful examination of the convergence properties of the expansion is necessary whenever there are multiple scales in the problem. Bender [19] has recently revisited the problem of correlated limits of multiple energy scales, in which the same variable is involved in more than one limit, in terms of \mathcal{PT} symmetry, while a recent study studying correlated limits in \mathcal{PT} -symmetric systems
 40 [20] numerically found that the apparent phase depends on the path taken towards the limits.

We show that the two expressions comprising the expression for superexchange, the singlet and triplet energies, possess different convergence properties, and as such, no single variable can reliably describe the limiting behaviour for
 45 superexchange. We also find that the series expansions used to obtain the limiting behaviour for superexchange are non-commuting, and that in a large part of parameter space, the reverse from the usual sequence of expansions yields better agreement with the exact expression. In Sec. 2 we outline our method of exact
 50 solution, and compare it with other methods, which are based on perturbation theory. The exact solution is expanded in different ways in Sec. 3 and compared with well-known limiting forms from the literature. A discussion is provided to explain the root of the discrepancies, and finally a summary is given in Sec. 4.

2. Theoretical Methods

2.1. Model of the system

55 We specifically consider the Wannier-orbital representation of Anderson's model of the MnO crystal [1], where in the ground state, unpaired $3d$ electrons on Mn are separated by O with a filled $2p$ shell. The system takes the form of a three-centre cluster model, as in Fig. 1. The $d - p$ energy difference, $\epsilon_d - \epsilon_p$, also known as the charge-transfer energy, has been defined as Δ .

To derive an expression for the exchange interaction between singly-occupied Mn cation sites, we use a two-band Hamiltonian of the Anderson-Hubbard type, given in second-quantized form by

$$H = \sum_{i,\sigma} (\epsilon_i - \mu) n_{i,\sigma} - t \sum_{\langle i,j \rangle, \sigma} \left(c_{i,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{i,\sigma} \right) + \sum_i U_i n_{i,\uparrow} n_{i,\downarrow} \quad (1)$$

where $\langle i, j \rangle$ denotes that the hopping with energy t is restricted to nearest neighbours, the ϵ_i term describes the on-site energy of an electron, and $n_{i,\sigma} \equiv c_{i,\sigma}^\dagger c_{i,\sigma}$ is the number of electrons of spin σ on site i . The presence of two electrons of opposite spin on a d orbital (Mn) comes at an energy cost U due to Coulomb repulsion; U_i for i corresponding to the central site, O, is taken to be zero. Finally, μ , taken to be equal to $(\epsilon_p + \epsilon_d)/2$, serves to shift the zero of energy. The Hamiltonian Eq. (1) may be depicted in tri-diagonal block form:

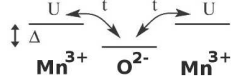


Figure 1: Site-centred Wannier orbitals in MnO and their associated energies. The site energy difference Δ (charge-transfer energy) is defined as $\epsilon_d - \epsilon_p$. For double occupation, there is a U only for the Mn d orbitals and none for the O p orbital.

$$H = \left(\begin{array}{c|c|c} H_{00} & T_{01} & 0 \\ \hline T_{10} & H_{11} & T_{12} \\ \hline 0 & T_{21} & H_{22} \end{array} \right) \quad (2)$$

with the nine anti-ferromagnetic basis configurations (sufficient for finding exchange) for four electrons on three sites,

$$\begin{aligned} \text{row 0 :} & \quad | \uparrow, \uparrow\downarrow, \downarrow \rangle, | \downarrow, \uparrow\downarrow, \uparrow \rangle \\ \text{row 1 :} & \quad | \uparrow\downarrow, \uparrow, \downarrow \rangle, | \uparrow\downarrow, \downarrow, \uparrow \rangle, | \uparrow, \downarrow, \uparrow\downarrow \rangle, | \downarrow, \uparrow, \uparrow\downarrow \rangle \cdot \\ \text{row 2 :} & \quad | \uparrow\downarrow, \cdot, \uparrow\downarrow \rangle, | \uparrow\downarrow, \uparrow\downarrow, \cdot \rangle, | \cdot, \uparrow\downarrow, \uparrow\downarrow \rangle \end{aligned} \quad (3)$$

⁶⁰ The unperturbed basis functions of block H_{00} have an energy of zero because of shift of the energy zero with μ as discussed above.

2.2. Effective Hamiltonian approach

We employ the formalism of the effective Hamiltonian, derived *exactly*, for the calculation of superexchange. The purpose of defining an effective Hamiltonian is to describe the full Hamiltonian in terms of a small subset of the basis, which for our purposes, is the H_{00} block (see Eq. (2)) as we are interested in the superexchange interaction between singly-occupied cation orbitals separated by O. An exact projection may be obtained from a resolvent approach (*e.g.* Ref. [21]). The solution, in terms of the notation of Eq. (2), is given by

$$\underline{H_{\text{eff}}}(E) = \underline{H_{00}} + \underline{T_{01}} \left(\underline{E} \underline{I_{11}} - (\underline{H_{11}} + \underline{T_{12}} (\underline{E} \underline{I_{22}} - \underline{H_{22}})^{-1} \underline{T_{21}}) \right)^{-1} \underline{T_{10}} \quad (4)$$

where I_{nn} is the identity matrix of the nn diagonal block of Eq. (2) and the matrix notation will be omitted hereafter for clarity. Our eigenvalue problem thus becomes

$$H_{\text{eff}}(E)X = EX, \quad X = |\uparrow, \uparrow\downarrow, \downarrow\rangle \pm |\downarrow, \uparrow\downarrow, \uparrow\rangle \quad (5)$$

for the projection onto singlet and triplet combinations of separated d electrons.

The undetermined E , appearing on both sides of Eqs. (4)-(5), can lead to the exact eigenvalue for *one* element i at a time in X if we solve for the roots of the equation $\lambda_i(E) = E$ for each corresponding eigenvalue $\lambda_i(E)$ of $H_{\text{eff}}(E)$. We essentially have two H_{eff} , for all of the eigenvalues of the singlet and triplet subspaces respectively. The difference in the lowest singlet and triplet energies, $E(S) - E(T)$, is defined as the superexchange J .

The formalism of the effective Hamiltonian is invoked here for two reasons. The first is to compare the results with the frequent implementation of using one effective Hamiltonian to describe all solutions within an energetically-degenerate subspace [22, 23] by approximating the unknown energy E in Eqs. (4)-(5) by the unperturbed energy, as in Rayleigh-Schrödinger perturbation theory. When followed by an expansion for small t , this leads to the same result as a T -matrix expansion with the unperturbed energy. The limitations of using unperturbed energies in Brillouin-Wigner perturbation theory to derive effective Hamiltonians have been previously noted [24]. The correspondence between resolvent

methods, which we have used, and Brillouin-Wigner perturbation theory, in
80 the derivation of effective Hamiltonians has been discussed extensively in *e.g.*
Refs. [21] and [25]. The second reason for projecting onto the model subspace
is technical: the particular splitting beforehand into two symmetry subspaces,
singlet and triplet, enabled MATHEMATICA [26] to find the required roots in
closed form.

85 3. Results

In this section, the exact, closed-form expressions for $E(S)$, $E(T)$, and J
provided by the effective-Hamiltonian formalism will be expanded in various
limiting forms.

3.1. Limiting forms for $U \gg t$

90 The expansion of the exact lowest triplet and singlet energy eigenvalues for
 $U \gg t$ up to $O(t^4)$ is

$$\begin{aligned} E(T) &= \left(\frac{2\Delta^3}{U^4} - \frac{2\Delta^2}{U^3} + \frac{2\Delta}{U^2} - \frac{2}{U} \right) t^2 + \left(\frac{4}{U^3} - \frac{12\Delta}{U^4} \right) t^4 + O(t^6) \\ E(S) &= \left(\frac{2\Delta^3}{U^4} - \frac{2\Delta^2}{U^3} + \frac{2\Delta}{U^2} - \frac{2}{U} \right) t^2 + \left(\frac{8\Delta}{U^4} - \frac{4}{U^3} \right) t^4 + O(t^6) \end{aligned} \quad (6)$$

such that

$$J = \frac{4t^4(5\Delta - 2U)}{U^4}. \quad (7)$$

Equations (6)-(7) were derived by substituting for $U \rightarrow t/x$ in the exact J and
expanding about x . The same result is obtained for $U \rightarrow \infty$ for up to $O(1/U^4)$
(single-scale limit).

On the other hand, setting $t \rightarrow Ux$ gives a totally different result:

$$J = \frac{-4(\Delta + 2U)t^4}{U(\Delta + U)^3}. \quad (8)$$

95 The expression (8) agrees with that obtained from expanding the exact J in the
single-scale series in $t \rightarrow 0$, but only up to fourth order - at higher order the
expressions differ. The result (8) is widely used for the $t \ll U$ situation (see *e.g.*
Eq. 13 in Ref. [2], and Eq. 16 in Ref. [4]), and it is often used as is, to describe

either the M-H case $\Delta > U$, [2, 3, 7] or the C-T case $\Delta < U$ [4, 7] without
 100 further, unrealistic limits relating Δ to U considered.

In deriving Eqs. (7)-(8), no assumptions have been made for Δ and yet, as
 can be seen from Fig. 2, although the two expressions coincide for very small
 Δ , for increasing Δ Eq. (7) poorly represents J as it increases without bound
 (except for the trivial case $U = \infty$ where it correctly gives zero). On the other
 105 hand, the convergence of the expansion leading to Eq. (8) improves as Δ is
 increased. Thus, even though Eq. (8) seems better than Eq. (7), in both cases,
 the convergence of the t/U expansion is impacted by the value of Δ . This concept
 of parameter-dependent convergence and its consequences will be discussed in
 detail in Sec. 3.4.

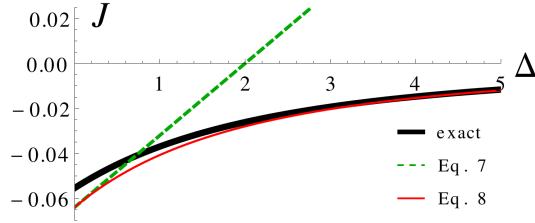


Figure 2: For fixed $t = 1, U = 4$, the variation of J with Δ in the exact form, and $t \ll U$
 according to the two approximation methods, leading to Eqs. (7) and (8) respectively.

If, instead of using the exact E in Eq. (4), the unperturbed energy is used,
 as described in Sec. 2.2, we obtain, without further approximations,

$$J = \frac{-4t^4(\Delta + 2U)}{(\Delta + U)(\Delta^2 U + 2\Delta(U^2 - t^2) - 4t^2 U + U^3)}. \quad (9)$$

110 The same expressions as Eq. (7) or (8) are obtained - with the agreement stop-
 ping after fourth order - upon setting $U \rightarrow t/x$ or $t \rightarrow Ux$ respectively and
 expanding about $x = t/U$ (or by defining $x = t/\Delta$). When $t \rightarrow Ux$ is set,
 the results are exactly the same to all orders as a T-matrix expansion with the
 unperturbed energy. On the other hand, taking the series expansion $U \ll \Delta$ of
 115 Eq. (9) does not lead to the results presented in Sec. 3.3 for the $U \ll \Delta$ limit of
 the exact J ; the validity of the perturbation expansion requires that t be “much
 smaller” than all of the other energy scales in the problem and the convergence

of $U \ll \Delta$ is mostly incompatible with this.

3.2. Anderson expression

The usual “Anderson” expression for superexchange [1] can be derived by considering the $U \ll \Delta$ limit of expression (8), yielding, in terms of the direct-exchange term $J_{dir} = -4t^2/U$ connecting $d-d$ nearest neighbours:

$$J_{\text{Anderson}} = \frac{J_{dir}t^2}{\Delta^2}. \quad (10)$$

Equation (10) was obtained with $\Delta \rightarrow U/x$ and expanding about x up to second order. On the other hand, the substitution $U \rightarrow \Delta x$ and expanding about x up to second order. On the other hand, the substitution $U \rightarrow \Delta x$ into Eq. (8) yields the modified expression, to first order,

$$J_{\text{Anderson } 2} = \frac{J_{dir}t^2(\Delta - U)}{\Delta^3} \quad (11)$$

(see also Ref. [11] Eq. 7 in slightly different notation) which leads Eq. (10) by two orders of expansion. The result (11) also arises from setting $t \rightarrow xU$ followed by $U \rightarrow y\Delta$ in the exact J , and expanding in x and y simultaneously, indicating that the neglect of mixed derivatives does not affect the result. However, the result remains intrinsically biased by the form of the substitution: expanding the series separately entails substituting back for the first expansion variable before proceeding to the second expansion.

3.3. $U \ll \Delta$ expansion

Rather than begin with small t , we first expand the exact J in $U \ll \Delta$ using $U \rightarrow \Delta x$ as in the “Anderson 2” expression Eq. (11). We expand up to $O(x^4)$. The result, although in closed form, is very unwieldy. For large t the expansion is accurate, but for small t it diverges for all but the smallest values of U as can be seen from Fig. 3. This shows explicitly that the U/Δ expansion is parameter-dependent. The $t \ll U$ expansion (Eq. (8)) is also shown for comparison, even though it is not expected to hold for $t > U$. Extrapolating beyond (c) for even larger t , the U/Δ expansion is found to be very accurate, even for $U > \Delta$.

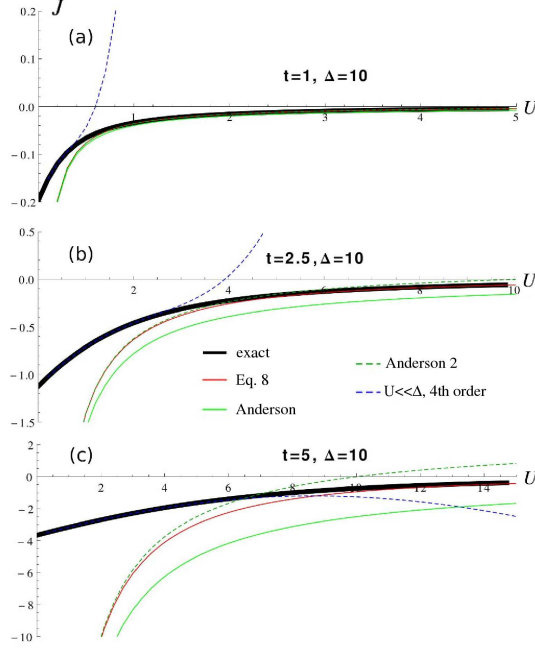


Figure 3: The variation of J with U for fixed $\Delta = 10$ and different values of t , in the exact form and in the limiting cases $t \ll U$ (Eq. (8)), the $U \ll \Delta$ limit of $t \ll U$ (“Anderson” case, (Eq. (10))) and “Anderson 2” (Eq. (11)), and $U \ll \Delta$ as discussed in the text.

The limiting forms Eqs. (8), (10)-(11), provided that $t \ll U \ll \Delta$ is strictly adhered to, lead to an accurate result for J . However, the meaning of the term ‘strictly’ here is vague because, as will be discussed in greater detail in Sec. 3.4, the two series expansions are correlated and this impacts the convergence, causing it to be parameter-dependent.

These limiting forms are worse than the $U \ll \Delta$ expression for cases in which the milder relationship $t \lesssim U \lesssim \Delta$ holds. Here, the $U \ll \Delta$ expansion coincides with the exact value. For instance in Fig. 3(c), a value of $J = -3.5$ is reached with $U=7.1$, 4.5, and 0.3 for the Anderson, Eq. (8), and $U \ll \Delta$ expressions respectively, causing the M-H relationship $t < U < \Delta$ to be fictitiously satisfied with the use of the Anderson expression. U obtained from the exact J is the same as that from the fourth-order $U \ll \Delta$ expression for this case. Similarly, for Fig. 3(b), for a measured $J = -0.3$, the values are $U=5.2$, 3.6, and 3.1

respectively, such that the qualitative relationship $t < U < \Delta$ is correctly
 150 determined, but with an inaccurate U in the Anderson model. Fig. 4(a) shows
 another perspective, that for $t \lesssim U$ the fitting of J to the model of Eq. (8), as
 opposed to the $U \ll \Delta$ limiting form, can give a value for Δ much larger than
 the correct one. Yet another depiction (Fig. 4(b)) shows how the deduced t can
 be far from the correct value when $t \lesssim U \lesssim \Delta$, and more importantly, that
 155 expanding the exact J with $U \ll \Delta$ is more accurate than using $t \ll U$.

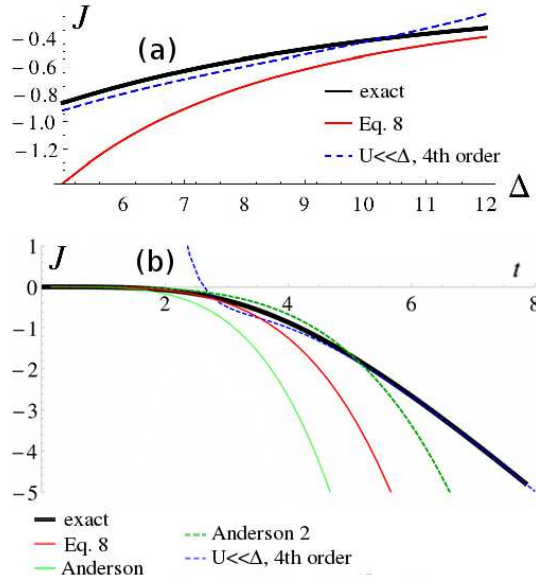


Figure 4: (a) the variation of J with Δ for $t = 3$, $U = 4$, and (b) the variation of J with t for $U = 6$, $\Delta = 8$. The various curves denote the exact form, the limiting cases for $t \ll U$ (Eq. (8)), the Anderson expressions Eqs. (10) and (11), and $U \ll \Delta$.

If the limits $U \ll \Delta$ and $t \ll U$ were in fact interchangeable, then Eq. (11),
 which was also derived with $U \rightarrow \Delta x$, would agree with the corresponding
 curve (first-order expansion in U/Δ followed by fourth-order expansion in t/U)
 of Fig. 5. In both cases, the variable substitutions were performed in exactly the
 160 same way - only the order of the expansions is reversed. It is clear from Fig. 5
 that the convergence with increasing order cannot be ensured, something found
 to occur also with other parameter values and types of depictions. The second

and fourth-order U/Δ expansions, without further limits taken, are quite reliable for certain regions of parameter space, often better than the t/U expansions, but for lack of representation by simple expressions they have to be used in their cumbersome forms. Although the t/U expansions of the $U \ll \Delta$ curves do have simple forms, such expressions would be worthless, as can be seen from Fig. 5. Incidentally, neither in the C-T insulator $t \ll \Delta \ll U$ situation, do the limits commute and similar conclusions can be made.

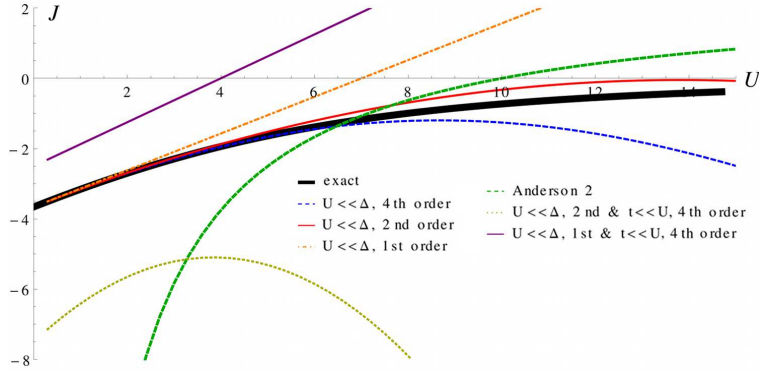


Figure 5: The variation of J with U for $t = 5$ and $\Delta = 10$, (as in Fig. 3(c)) in the exact form and in various limiting cases. Specifically, expansions beginning with the $U \ll \Delta$ limit, some followed by a further expansion with $t \ll U$, are shown alongside the “Anderson 2” expression, Eq. (11), which arises from the reverse order of two expansions: $t \ll U$ first and then $U \ll \Delta$. See text for more details.

The disagreement in the results depending on the sequence in which the expansions are taken means that the limit is formally undefined. This manifests itself as a better agreement of the $U \ll \Delta$ expression with the exact result for the milder limits compared with the results derived starting with $t \ll U$, due to a divergence of the latter with increasing expansion order in this region (Fig. 6).

3.4. Radius of convergence

The inconsistency between the two types of expansion procedures (*e.g.* leading to Eqs. (7) and (8) respectively) is due to the radius of convergence (ROC) being unstable due to the multiple variables and due to the fractional powers

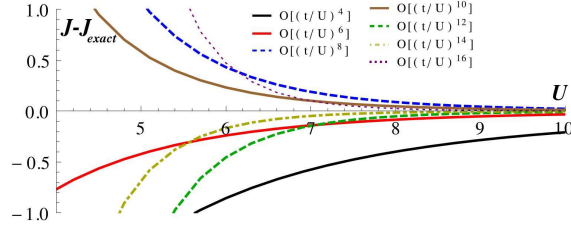


Figure 6: The difference of the approximate J in its various orders of expansion in t/U (or t/Δ , with the same result) from the exact value, as a function of U for fixed $t = 5$, $\Delta = 10$ (as in Figs. 3(c) and 5).

present in the function. Consider the triplet energy, which has the simple form

$$E(T) = \frac{1}{2} \left(\Delta + U - \sqrt{\Delta^2 + 2\Delta U + 8t^2 + U^2} \right). \quad (12)$$

Substituting for t as $t \rightarrow xU$ yields one form for the series, while another form is found with $U \rightarrow t/x$. The first form has a ROC which is dependent on $\frac{(U+\Delta)^2}{U^2}$, while in the second form there is an unstable parameter dependence with increasing series order. The ROC of both forms coincide and are parameter-free when $\Delta = 0$. The parameter-dependence of the ROC is the root cause of the limits $t \ll U$ and $U \ll \Delta$ of J being non-commuting; even in the simultaneous limits described earlier at the end of Sec. 3.2, the result was biased by the form of the substitution. The limits are “correlated” and this impacts the convergence condition.

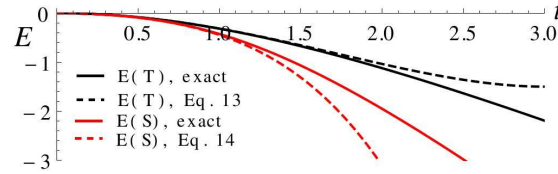


Figure 7: For fixed $U = 1$, $\Delta = 5$, the variation of the triplet and singlet eigenvalues with t in the exact form and in the approximate forms Eqs. (13)-(14).

Parameter-dependent ROC require that an additional condition be satisfied, in addition to the smallness of the expansion parameter. Together they yield an expansion variable $x^* = t/(\Delta + U)$ for $E(T)$ which yields global (parameter-

free) convergence for $x^* < \frac{1}{2\sqrt{2}}$. In the case of the singlet however, the ROC remains parameter-dependent and more restrictive. Up to fourth order in the expansion parameter x^* , we have deduced the expressions:

$$E(T) = -\frac{2t^2}{U+\Delta} + \frac{4t^4}{(U+\Delta)^3} \quad (13)$$

$$E(S) = -\frac{2t^2}{U+\Delta} - \frac{4t^4}{U(U+\Delta)^2}, \quad (14)$$

which result again in Eq. (8) for J , a ubiquitous expression also obtained with various other expansion parameters, such as $x = t^2/(U\Delta)$. It should be noted that the agreement between the various J expressions obtained with different expansion parameters is fortuitous, occurring only up to fourth-order in the expansion parameter; at higher order they differ. For $U = 1$, $\Delta = 10$, x^* gave $t/(U+\Delta) \lesssim 0.18$, or $t < 2.0$ for the singlet, compared with $t < 3.9$ for the triplet. Thus, U does not need to be larger than t for Eq. (8) to be accurate (see also Fig. 3(a) for this case). Figure 7 shows the difference in the convergence for $U = 1$ and $\Delta = 5$ for which the numerical evaluation gave $t < 2.1$ and $t < 1.3$ for the convergence condition of the infinite series expanded in x^* for $E(T)$ and $E(S)$ respectively. Clearly, J is composed of two functions with different convergence properties.

4. Conclusions

We have shown that the commonly referred-to Mott-Hubbard (M-H) insulator situation, $t \ll U \ll \Delta$ yields the Anderson form for superexchange only if the limits are taken in a particular sequence. Hence, the limit is actually undefined (also true for the charge-transfer (C-T) insulator) and the reason for this is the incompatibility of the expansion variables with the radius of convergence, which depends on the parameters appearing in the problem. The Anderson expression, or other limiting expressions, derived *e.g.* from $t \ll U$, but also from many other parameter relationships, agree very well with the exact result in the extreme form of these limits. However, for milder relationships between the

parameters, *e.g.* $t < U < \Delta$, the limiting form $t \ll U$ can be significantly less accurate than the oppositely-derived limit $U \ll \Delta$.

215 The M-H limits, which arise from the convenience of the application of perturbation theory, represent a subset of the range of applicability of the limiting form as we found that other expansions, which assume different relationships between the variables, *e.g.* $U < t$, yield the same limiting form of J to great success. We additionally show that since the triplet and singlet energies comprising J display different convergence properties, a single expansion variable
220 for determining J does not formally exist.

The wider implications of our findings are that the results determined for electronic parameters, and the quantities derived from them such as electron transfer rates, could be questionable if an approximate expression for J instead
225 of the exact result is relied upon. This is because the parameters found from fitting to experimental data could be outside the radius of convergence of the series, particularly when the parameters do not hold extreme relationships amongst themselves and this may yield a fictitious qualitative relationship between the parameters. As in previous works, [16–18] where more detailed calculations, taking into account higher-energy excitations, have been shown to modify the
230 characterization (*e.g.* from M-H to C-T insulators) of some transition-metal oxides, here as well, through exact solutions of a simpler model system, we are able to show that the classification of materials obtained by models based on perturbative approaches can be modified in regimes where such methods break
235 down.

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